

Graft Polymerization of Acrylonitrile onto Wheat Straw

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Synopsis

Acrylonitrile was graft polymerized onto ground, water-washed wheat straw using Fe^{2+} - H_2O_2 as initiator. Reaction conditions were selected to minimize homopolymer formation and maximize the amount of polyacrylonitrile (PAN) grafted to straw. Polymerizations typically yielded straw-*g*-PAN containing 30–35% PAN. A two-step fractionation scheme was developed for determining the relative amounts of PAN grafted to cellulose, hemicellulose, and lignin. This scheme involved (1) delignification of straw-*g*-PAN with sodium chlorite followed by removal of lignin-grafted PAN by extraction with dimethylformamide (DMF), and (2) hydrolysis of the hemicellulose component with 1 *N* trifluoroacetic acid followed by DMF extraction of hemicellulose-grafted PAN. Product remaining after these two treatments was assumed to be cellulose-*g*-PAN. When relative amounts of PAN grafted to cellulose, hemicellulose, and lignin were compared with relative percentages of these components present in wheat straw, the percentage of total PAN grafted to lignin was less than its relative percentage in straw, whereas that grafted to hemicellulose was considerably more. Although the use of Ce^{4+} as initiator gave little or no polymer with whole, water-washed straw, graft polymerization occurred when delignified straw was used as substrate. Relative amounts of PAN grafted to cellulose and hemicellulose were not greatly different from those observed with Fe^{2+} - H_2O_2 initiation onto whole straw.

INTRODUCTION

Living plants constitute some of the most complex and best formulated polymeric composites known. Although plant-derived polymers have unique properties that are difficult to duplicate synthetically, such drawbacks as water sensitivity and high softening temperature make them unsuitable for some uses, and these applications are at present served by synthetic polymers derived from petrochemicals. Graft polymerization onto plant-derived materials is one method for modifying some of their undesirable properties, and much has been published on both starch¹ and cellulose^{2,3} grafting. Graft polymerizations onto lignocellulosic materials derived from a number of different plant sources have also been reported.⁴

Graft polymerization onto whole plant materials is less common in the literature, and major contributions in this category have been in the area of wood-plastic composites.^{5,6} Although there have been reports on graft poly-

*The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

merizations onto cereal straw,⁷ this subject has not received an amount of study commensurate with the abundance of straw as a source of biomass. Also, the literature provides no information on percentages of total grafted polymer bound to the major straw components (cellulose, hemicellulose, and lignin).

In this report, we will examine graft polymerizations of acrylonitrile onto wheat straw. Acrylonitrile was chosen because it readily graft polymerizes onto starch,¹ cellulose,² and hemicellulose⁸ in the presence of a number of different initiating systems. Moreover, final products should have potential utility, since saponification of polysaccharide-*g*-polyacrylonitrile (PAN) produces a copolymer having both water absorbent and thickening properties.⁹ Our work will center on a study of reaction conditions, which we screened to maximize the amount of PAN incorporated in the graft copolymer, and on the development of a fractionation scheme to provide information on relative amounts of PAN grafted to the three major straw components.

EXPERIMENTAL

Materials

Straw of soft winter wheat (*Triticum aestivum*, variety Arthur) from central Illinois was freed of heads, roots, and leaves and was ground in a Wiley mill (screen with 2 mm round openings). Ground straw was washed eight times with water at room temperature (100 g straw in 3 L) and was allowed to air-dry to a moisture content of about 8%. Weight loss was 13–14%. Nitrogen analysis of washed straw was 0.2%.

Acrylonitrile (Eastman) was distilled at atmospheric pressure through a 14 inch Vigreux column. Hydrogen peroxide (30%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, and ceric ammonium nitrate were Fisher Certified ACS grades.

Graft Polymerization

After 5 g of straw in 100 mL of water was acidified with sulfuric acid, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added as a 2% aqueous solution, and the resulting stirred mixture was sparged with a slow stream of nitrogen for 1 h. Acrylonitrile was added followed after 5 min by hydrogen peroxide, and the mixture was stirred for 3 h. Polymer was separated by filtration, washed with water, and allowed to air-dry at room temperature. Homopolymer was removed by repeated extraction at room temperature with dimethylformamide (DMF), and the percentage of PAN in the final air-dried product (percentage add-on) was calculated either from weight gain or from Kjeldahl nitrogen analysis, after applying the appropriate correction for moisture.

For ceric-initiated grafting onto delignified¹⁰ wheat straw, 15.0 g of acrylonitrile was added to a nitrogen-sparged suspension of 15.0 g of straw in 300 mL of water. After 5 min, a solution of 0.5 g of ceric ammonium nitrate in 5 mL of 1 *N* nitric acid was added and the mixture was stirred for 3 h at room temperature. The yield of air-dried polymer was 25.6 g (5–10% moisture content). DMF extraction removed 5.8 g of homopolymer; the remaining straw-*g*-PAN contained 16.6% PAN.

Fractionation of Straw-*g*-PAN

Straw-*g*-PAN was delignified with sodium chlorite,¹⁰ and the air-dried product was extracted with several portions of DMF to remove the PAN that was originally bonded to lignin. A 5 g portion of the DMF-insoluble fraction was next refluxed in 50 mL of 1 *N* trifluoroacetic acid (TFA) for either 15 min or 2 h to hydrolyze the hemicellulose component. Polymer was separated by filtration, washed with water, and air-dried at room temperature. Repeated extraction with DMF removed the PAN that was originally bonded to hemicellulose, leaving cellulose-*g*-PAN as a fibrous solid insoluble in DMF. PAN contents of all fractions were calculated from Kjeldahl nitrogen analyses.

Molecular Weights of PAN Grafts

DMF-soluble PAN fractions with either hemicellulose or lignin end groups were further purified by dissolving them in DMF, evaporating the resulting solutions to near dryness, and precipitating the polymers with 0.5 *N* HCl. Freshly precipitated polymers were heated under reflux in 0.5 *N* HCl for 1.5 h, washed with water and with ethanol, and dried. Lignin-grafted PAN was also washed with 95 : 5 chloroform-methanol to further remove any organic-soluble lignin fragments. Polymers were dissolved again in DMF, small amounts of insolubles were removed by either centrifugation or filtration, and polymers were isolated again by precipitation and water washing. Infrared spectra were nearly identical with that of pure PAN. Molecular weights of PAN grafts were calculated from intrinsic viscosities in DMF.¹¹

In contrast to earlier work with bleached wood pulp-*g*-poly(methyl acrylate),¹² cellulose could be only partially removed from a cellulose-*g*-PAN fraction by the sodium periodate-sodium methoxide procedure.⁸ Further treatment with HCl in ZnCl₂ solution¹³ was also unsuccessful and gave a product (containing roughly 20% residual polysaccharide) that was largely insoluble in DMF.

RESULTS AND DISCUSSION

Graft polymerizations of acrylonitrile onto ground, water-washed wheat straw were initiated with the ferrous sulfate-hydrogen peroxide redox system. Water washing was a necessary first step, since unwashed straw showed little reactivity. Attempts to initiate polymerizations with ceric ammonium nitrate and with cobalt 60 resulted in little or no grafting, presumably due to the inhibiting effect of lignin.¹⁴ It is not clear, however, why initiation was not similarly inhibited with hydroxyl radicals generated from Fe²⁺-H₂O₂.

Initially, a number of small-scale polymerizations were carried out to determine how reaction variables influence the percentage add-on of straw-*g*-PAN and amount of homopolymer produced. Stepwise increases in FeSO₄ · 7H₂O from 0.01 g to 0.1 g per 5 g of straw at pH 3.5 and at 35°C (Table I) produced corresponding increases in homopolymer, and the percentage add-on reached a maximum of 28% with 0.05 g of FeSO₄ · 7H₂O. No reaction occurred in the absence of ferrous ion. With 0.05 g of FeSO₄ · 7H₂O, gradually decreasing the initial pH from 4.5 to 2.3 increased homopolymer yield from 0.4 to 6.8 g but caused only small variations in the percentage

TABLE I
 pH and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ as Variables^a

Initial		g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	g Product ^b	% PAN in Product ^c	g DMF Sol. (homopolymer)
xp	pH				
09	3.5	0	< 5	0	—
10	3.5	0.010	5.78	13	0.2
12	3.5	0.025	6.54	24	1.8
14	3.5	0.050	6.95	28	5.0
07	3.5	0.10	6.90	28	5.9
16	4.5	0.050	6.62	25	0.4
20	4.3	0.050	6.85	27	1.6
23	2.3	0.050	6.55	24	6.8

^a Polymerizations run for 3 h at 35° C with 5 g straw, 100 mL water, 10 g acrylonitrile, and 1 g 30% H_2O_2 ; pH adjusted with H_2SO_4 .

^b After extraction of homopolymer with dimethylformamide.

^c Calculated from weight gain after extraction of homopolymer with dimethylformamide.

 TABLE II
 Acrylonitrile (AN), Hydrogen Peroxide, and Temperature as Variables^a

xp	g AN	g 30% H_2O_2	Polymerization		% PAN in Product ^c	g DMF Sol. (homopolymer)
			temperature (°C)	g Product ^b		
37	10	1	25	6.39	22	1.4
20	10	1	35	6.85	27	1.6
35	10	1	45	7.32	32	1.5
42	10	1	55	7.99	37	1.4
32	15	1	35	7.05	29	0.9
30	10	2	35	6.73	26	1.4

^a Polymerizations run for 3 h with 5 g straw and 0.050 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Reactions run in 100 mL of 0.001 M H_2SO_4 (initial pH 4.3).

^b After extraction of homopolymer with dimethylformamide.

^c Calculated from weight gain after extraction of homopolymer with dimethylformamide.

add-on. Perhaps the best balance between high add-on and low homopolymer yield was thus obtained in experiment 20, in which an initial pH of 4.3 was achieved by running the polymerization in 0.001 M sulfuric acid with 0.05 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. In a series of polymerizations under these conditions (Table II), increasing the reaction temperature from 25 to 55° C increased add-on from 22 to 37% without greatly changing homopolymer content. Increases in acrylonitrile (experiment 32) and hydrogen peroxide (experiment 30) did not produce significant changes in the percentage add-on or homopolymer.

Two polymers in Table II were selected for determination of relative amounts of PAN grafted to cellulose, hemicellulose, and lignin: experiment 20, run at 35° C (polymer I), and experiment 42, run at 55° C (polymer II). To provide sufficient straw-g-PAN for fractionation, reactions were scaled up by a factor of 3. The scheme used for fractionation (Fig. 1) involved two steps: (1) delignification of straw-g-PAN via the well-known sodium chlorite procedure¹⁰ followed by extraction of lignin-grafted PAN with DMF, and (2) hydrolysis of the hemicellulose component with refluxing 1 N TFA followed by DMF

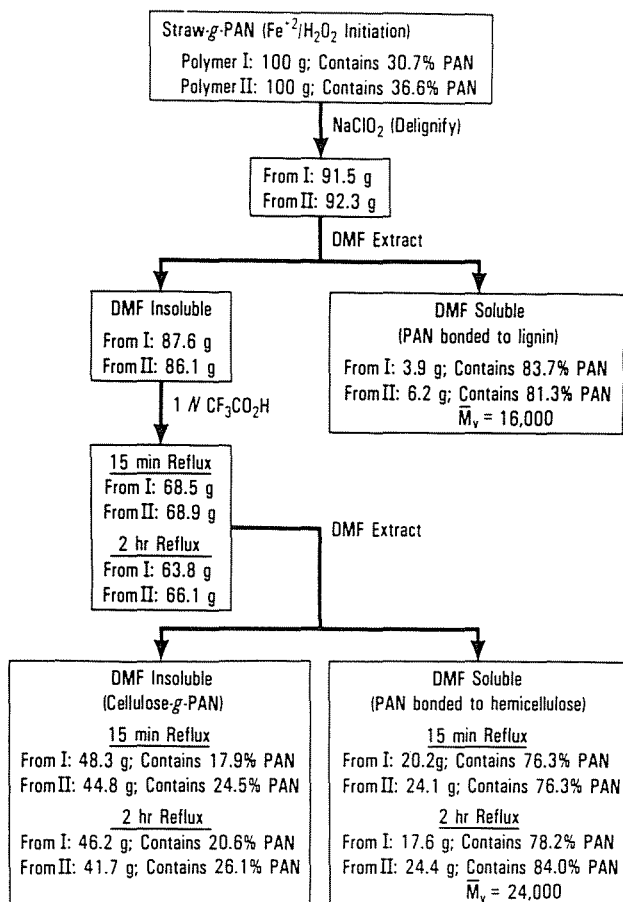


Fig. 1. Fractionation scheme for straw-g-PAN prepared from whole straw with Fe^{2+} - H_2O_2 initiation. Polymers I and II are three-fold scaleups of experiments 20 and 42, respectively.

extraction of hemicellulose-grafted PAN. Previously,¹⁵ we showed that 1 *N* TFA selectively hydrolyzes hemicellulose in straw to monosaccharides without converting cellulose to glucose. The product remaining after these two treatments was assumed to be cellulose-g-PAN. PAN contents of each fraction were calculated from nitrogen analyses, and all weights given in Figure 1 were normalized to 100 g of starting straw-g-PAN. Values in Figure 1 were then used in Table III to calculate the relative percentages of PAN grafted to each of the three major straw components.

Several factors can affect the accuracy of our results. In step 1 of our scheme, we considered the possibility that treatment of straw-g-PAN with sodium chlorite might not only degrade lignin but might also partially degrade cellulose and hemicellulose, thus allowing some polysaccharide-grafted PAN to be removed by DMF extraction along with the lignin grafts. To test for this side reaction, we prepared a graft copolymer containing 20% PAN from bleached softwood pulp having a lignin content of only 0.06%. Treatment of this model graft copolymer with sodium chlorite and then extracting it with DMF removed about 5% of the total PAN present. Because of prior bleaching,

TABLE III
Percentage of Total Polyacrylonitrile Grafted to Cellulose, Hemicellulose,
and Lignin Components of Wheat Straw

		Percentage of total grafted PAN	
		Based on 15-min reflux (1 N TFA ^a)	Based on 2-h reflux (1 N TFA)
Polymer I ^b	Cellulose-grafted	32	36
	Hemicellulose-grafted	56	52
	Lignin-grafted	12	12
Polymer II ^c	Cellulose-grafted	32	30
	Hemicellulose-grafted	53	56
	Lignin-grafted	15	14
Polymer from delignified straw (Ce ⁴⁺) ^d	Cellulose-grafted	39	41
	Hemicellulose-grafted	61	59

^a TFA: Trifluoroacetic acid.

^b A threefold scaleup of experiment 20, Table II. Percentages calculated from Figure 1.

^c A threefold scaleup of experiment 42, Table II. Percentages calculated from Figure 1.

^d Percentages calculated from Figure 2.

polysaccharides in our model graft copolymer are probably more susceptible to sodium chlorite degradation than those in straw-*g*-PAN.

We also recognized the possibility of incomplete degradation of lignin by sodium chlorite as a result of the graft polymerization reaction. The presence of some incompletely degraded lignin, however, should not prevent the extraction of lignin-grafted PAN with DMF. Since it is known¹⁶ that grafted branches of synthetic polymer can carry a significant percentage of chemically attached polysaccharide into solution when the graft copolymer is in contact with an organic solvent for the synthetic polymer moiety, we envisage a similar behavior of PAN with lignin end groups.

In step 2 of our scheme, it seemed possible that slight hydrolysis of cellulose could occur in refluxing 1 N TFA, thus permitting extraction of some cellulose-*g*-PAN by DMF along with hemicellulose-derived PAN grafts. Both of our delignified straw-*g*-PAN polymers were, therefore, subjected to two sets of hydrolysis conditions, which differed greatly in severity: 15 min reflux and 2 h reflux in 1 N TFA. Since Table III shows that these two sets of conditions give about the same calculated percentages of PAN grafted to cellulose, hemicellulose, and lignin, cellulose degradation by refluxing 1 N TFA appears not to be a significant side reaction.

Examination of Table III shows that most of the PAN grafted to wheat straw is bound to the hemicellulose component, and bonding to lignin represents the smallest percentage of the total grafted PAN. Relative percentages were not greatly different for polymers I and II. If we consider the published composition of wheat straw¹⁷ and ignore inorganic components and low-molecular-weight organic solubles, we can calculate relative percentages of 42, 39, and 19 for cellulose, hemicellulose, and lignin, respectively. When we compare these calculated values with percentages of PAN grafting observed in Table III, it is apparent that PAN grafting to lignin is less than expected, whereas

the amount grafted to hemicellulose is considerably more than its relative abundance in straw.

A number of explanations can be given for the grafting percentages given in Table III. Reduced grafting to lignin might be caused by the free radical chain inhibiting potential of phenolic groups, whereas another possibility is that DMF extraction of straw-*g*-PAN prior to fractionation may simply have removed some lignin-*g*-PAN along with homopolymer. The partial crystallinity of cellulose is a possible explanation for the low cellulose-hemicellulose grafting ratio. Since grafting should occur chiefly in amorphous regions,¹⁸⁻²⁰ the presence of crystallinity would have the same effect as reducing the concentration of cellulose in the straw composite.

The molecular weights of PAN grafts given in Figure 1 were determined by intrinsic viscosity after the removal of residual polysaccharide or lignin from selected polymer fractions. M_v values for hemicellulose- and lignin-grafted PAN were low (24,000 and 16,000, respectively). The M_v for cellulose-grafted PAN was not determined owing to the small samples available and the difficulty encountered in completely removing polysaccharide from PAN (see Experimental).

We mentioned earlier that little or no grafting onto straw takes place with ceric initiation, presumably owing to the inhibiting effect of lignin. However, when a sample of straw was first delignified with sodium chlorite¹⁰ and then subjected to ceric-initiated grafting, polymerization with acrylonitrile occurred readily, although a 39% conversion of monomer to homopolymer was produced and the graft copolymer contained only 16.6% PAN. This high conversion to homopolymer was unexpected, based on our earlier work with starch.¹

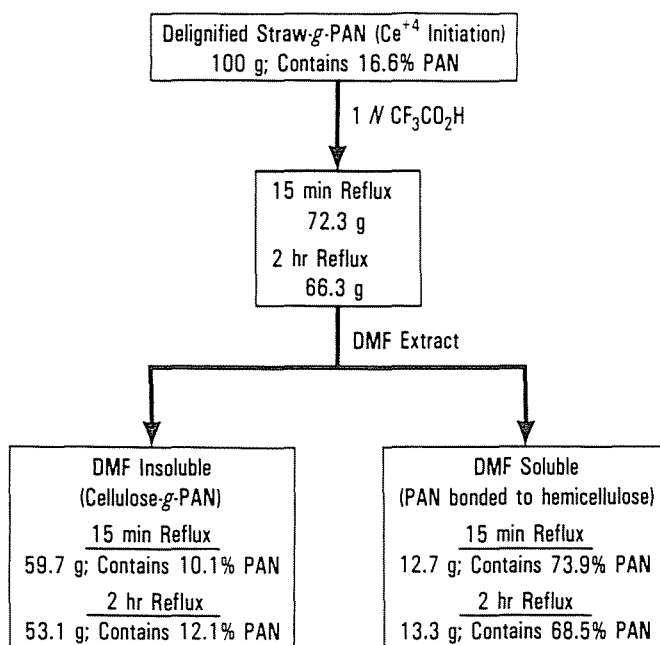


Fig. 2. Fractionation scheme for straw-*g*-PAN prepared from delignified straw with Ce^{4+} initiation.

Moreover, a similar polymerization carried out with bleached softwood pulp as the substrate gave a graft copolymer with 40% add-on and only a 7% conversion to homopolymer. The reasons for these differences in grafting behavior are not known.

Samples of straw-*g*-PAN with 16.6% add-on were subjected to refluxing 1 *N* TFA for periods of 15 min and 2 h to separate hemicellulose-grafted PAN, which was then removed by DMF extraction. The results of this fractionation are summarized in Figure 2, and calculated percentages of PAN grafted to cellulose and to hemicellulose are given in Table III. As observed with Fe^{2+} - H_2O_2 initiation onto whole straw, values did not vary greatly with reflux time. Also, ratios of hemicellulose-grafted PAN-cellulose-grafted PAN were not greatly different for the two initiating systems.

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